FINAL PROJECT REPORT TO ONR

***In situ* Studies of Defect Nucleation During the PVT and CVD Growth of Silicon Carbide Single Crystals (N000140211014; Oct. 2002 – March 2006)**

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A complete chemical vapor deposition (CVD) system for growing SiC epitaxial films and bulk crystals was set up using commercially procured gas flow controls and scrubber units, and integrating them with a modified in-house designed growth chamber that has options for *in situ* X-ray topographic study. This CVD system uses silicon tetrachloride ($SiCl_4$), silane (SiH_4), propane (C_3H_8), hydrogen (H_2) and argon (Ar) gases. The aggressive $SiCl_4$ corrosion in the chamber and the gas lines has been investigated and found to be predominantly related to moisture, and this severe problem has been solved by keeping the gas lines and the growth reactor in vacuum or in inert atmosphere when the CVD the system is not running.

The hot-zone design and growth conditions have been optimized by using numerical modeling as well as thermodynamic modeling. Detailed numerical modeling showed how the temperature field contours get shifted towards the exit end of the hot-zone depending on the associated thermal capacity of the gases at different flow rates. Detailed experiments were performed in both the kinetically and thermodynamically controlled regions, achieved by altering the growth parameters, and the results compared with our equilibrium model. This enabled it to be determined that kinetically controlled CVD growth is more effective, and that 6H-SiC homo-epitaxial layers grown at about 1500°C in this condition resulted in high quality films in terms of surface morphology and lower basal plane dislocation density.

Thick films, up to 300 μm, of 6H SiC and 4H SiC could be grown using $SiCl_4$ and C_3H_8 precursors. The grown films have been subjected to various characterization procedures, in particular to the imaging of defects structure using X-ray topography and its variants. Grazing incidence and back reflection synchrotron X-ray topographs revealed the basal dislocations, threading screw dislocations in the entire area of the epitaxial layer and the substrate. Low basal plane dislocation density ($10^4/cm^2$) was observed in the epitaxial layer grown at slower rates (e.g. 5μm/hr). Most of these basal plane dislocations show predominantly edge character. KOH etching carried out on the epitaxial layer revealed low angle grain boundaries that consisted predominantly of threading edge dislocations. The threading edge dislocations and threading screw dislocations densities were $10^4/cm^2$ and $10^3/cm^2$, respectively. Suitable steps have been worked out to lower dislocation densities. In general, defects present in the substrate such as micropipes, threading dislocations and grain boundaries are found to replicate in the epitaxial layer. However, no additional micropipe nucleation was observed in the epitaxial layer. Some elementary screw dislocations present in the substrate found to disappear in the epitaxial layer, possibly due to some kind of conversion and/or annihilation mechanism. The dislocation densities primarily depended on the substrate quality. The rocking curve measurements show that in certain cases that structural quality of the epitaxial layer was better than the substrate itself when off-cut substrates were used. The growth rates were found to increase with the growth temperature. However, the growth rate reduced when the hydrogen flow rate was increased from 5 slpm to 15 slpm, which agrees well with our modeling. This effect also correlates well with the observation of shifting of the maximum temperature due to the gas flow effects from the modeling results. Good films, with superior surface quality containing lower dislocation density, were obtained at about 1500°C and above which the morphology becomes rough because of the simultaneously occurring hydrogen etching. A hydrogen defect etching process was developed to reveal micropipes and also obtain a quantitative measure of micropipes.

The CVD system was optimized and it could run reliably for 24 hours without any blocking effects in the hot-zone. Now the system is suitable for extending it to obtain mm size boules using halide precursor in the CVD system. *Ex situ* as well as model *in situ* studies carried out on the SiC samples grown at Stony Brook reveal a great potential for obtaining the insights of the defect nucleation and the crystal growth process. As a relevant part to this investigation, we also developed a geometrical model that clearly explains the conversion of basal plane dislocations into threading edge dislocations.

This ONR grant also resulted in manpower training. Two Ph.D students (Feng Liu, MS, 2003; Yi Chen MS, 2003, Ph.D, estimated 2007) and a postdoc (Dr. G. Dhanaraj) were employed on this project.

Publications Resulting from this Work:

1. Springer Handbook of Crystal Growth, Defects and Characterization. Eds: G. Dhanaraj, K. Byrappa, V. Prasad and M. Dudley (1800 pages) Springer (Heidelberg, Germany) 2007.
2. G. Dhanaraj, Y. Chen, H. Chen, D. Cai, H. Zhang and M. Dudley, Chemical Vapor Deposition of Silicon Carbide Epitaxial Films and Their Defect Characterization, Journal of Electronic Materials 2006 (in press)
3. Y. Chen, G Dhanaraj, W. Vetter, R. Ma and M. Dudley, Multiplication of Basal Plane Dislocations and Low Angle Grain Boundary Formation in Hexagonal Silicon Carbide, Materials Science Forum 2006 (in press)
4. Y. Chen, G Dhanaraj, H. Zhang and M. Dudley, Thermodynamic studies of carbon in liquid silicon, Journal of the American Ceramic Society **89** (2006) 2922
5. G. Dhanaraj, Y. Chen1, H. Chen, W.M Vetter, H. Zhang and M. Dudley, Growth mechanism and dislocation characterization of silicon carbide epitaxial films, MRS Proceedings **911** (2006) 0911-B05-27
6. Y. Chen, G. Dhanaraj, M. Dudley1, H. Zhang, R. Ma, Y. Shishkin, and S. E. Saddow, Multiplication of basal plane dislocations via interaction with c-axis threading dislocations in 4H-SiC, MRS Proceedings **911** (2006) 0911-B09-04
7. Y. Chen, G Dhanaraj, M. Dudley and H. Zhang, Chemical vapor deposition and defect characterization of silicon carbide epitaxial films, MRS Proceedings **819** (2005), 0891-EE12-11
8. B. Raghothamachar, G Dhanaraj, M. Dudley and B. Jie, X-ray topography and defect analysis in crystals, Microscopy Research and Technique **69** (2006) 343
9. G Dhanaraj, Y Chen, M. Dudley and H. Zhang, Growth and Surface Morphologies of 6H SiC bulk and epitaxial crystals, Materials Science Forum **527** (2006) 67
10. M. Dudley, J. Bai, X. Huang, W.M. Vetter, G. Dhanaraj and B. Raghothamachar "Synchrotron white beam X-ray topography, transmission electron microscopy and high resolution X-ray diffraction studies of defects and strain selaxation processes in wide bandgap semiconductor crystals and thin films", Materials Science in Semiconductor Process **9** (2006) 315

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12. J. Bai, G. Dhanaraj, P. Gouma, M. Dudley, and M. Mynbaeva, "Porous SiC for HT chemical sensing devices: an assessment of its thermal stability", Materials Science Forum **457** (2004) 1479
13. G. Dhanaraj, F. Liu, M. Dudley, F. Liu , H. Zhang and V. Prasad, PVT growth of 6H SiC crystals and defect characterization, MRS Proceedings **815** (2004) p. J5.31.1
14. Dhanaraj, M. Dudley, R-H. Ma, H. Zhang and V. Prasad, Design and fabrication of physical vapor transport (PVT) system for the growth of SiC crystals, Review of Scientific Instruments **75** (2004) 2843
15. M. Dudley, X.-R. Huang and W.M. Vetter, "Contribution of X-ray Topography and High Resolution Diffraction to the Study of Defects in SiC", **J. Phys. D., Appl. Phys., 36**, A30-A36, (2003).
16. M. Dudley, X Huang, W.M. Vetter, and P.G. Neudeck, "Synchrotron White Beam X-ray Topography and High Resolution Triple Axis X-ray Diffraction Studies of Defects in SiC Substrates, Epilayers and Devices", in *Silicon Carbide and Related Materials 2002,* P. Bergman and E. Janzen (Eds.), **Materials Science Forum, 433-436**, 247-252, Trans Tech Publications, Switzerland, (2003).
17. J. Hartwig, J. Baruchel, H. Kuhn, X.R. Huang, M. Dudley, and E. Pernot, "X-ray "Magnifying" Imaging Investigation of Giant Burgers Vector Micropipe Dislocations in 4H-SiC", **Nucl. Instr. & Meth., 200**, 323-328, (2003).